A Novel Concept of Symmetry in Real Fluids

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It is known that conventional statements of scaling theory are 1) the simple fluids belong to the lattice gas (LG) universality class; 2) the real fluids and van der Waals (vdW) models does not possess any immediately apparent symmetry and therefore the corrections to the asymptotic power laws and assymetry must be taken into account in the extended critical region. Contrary to this belief we would like to show that LG, vdW models and real fluids have a common line of symmetry – continuation of critical isochore by the line of rectilinear diameter $\rho_D = (\rho^l + \rho^g)/2$ which is consistent with scaling theory, but the separation from the critical point must be measured in terms of new parameter- the reduced difference of the specific entropies: $s = (s^g - s^l)M/2R$. Temperature dependence of parameter (s) can be obtained from the latent heat $r(T)$. A nearly ideal linear dependencies of the reduced densities: ρ^l/ρ_c, ρ^g/ρ_c and order parameter $(\rho^l - \rho^g)/\rho_c$ as a function of s were found for a set of well-studied fluids (N_2, CH_4, C_2H_4, CO_2, C_6H_{12}). It is interesting that parametric solution of of the vdW-Maxwell problem demonstrates the same symmetry and linearity in the similar range of coexistence curve. The symmetry in vdW model and the real fluids differ by the value of slopes of $\boldsymbol{\rho}(s)$ –linear dependencies for the coexisting phases. The slope is equal $\pm 1/2$ for the real fluids, $\pm 2/3$ for the vdW model and $\pm \infty$ for LG model. We conclude that the symmetry in real fluids are much more similar to the vdW model than to the LG-model, and therefore in order to achieve the adequate description of real fluids in the vicinity of critical point a combination of background (vdW-like) and scaling (LG-like) types of behavior should be taking into account. The above-discussed symmetry holds for the wide range of density $\rho = \rho_c \pm 0.3\rho_c$, which corresponds to the domain $s \leq 0.5$ of the new parameter.